

## Triplet Energy Transfers in Electrostatic Host–Guest Assemblies of Unsaturated Organometallic Cluster Cations and Carboxylate-Containing Porphyrin Pigments

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The unsaturated cyclic  $[M_3(\text{dppm})_3(\text{CO})]^{2+}$  clusters ( $M = \text{Pt}, \text{Pd}$ ;  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ; such as  $\text{PF}_6^-$  salt) exhibit a cavity formed by the six  $\text{dppm}$ -phenyl groups placed like a picket fence above the unsaturated triangular  $M_3$  dicationic center. Electrostatic interactions of the  $M^{3+}$  units inside this cavity with the carboxylate anion  $\text{RCO}_2^-$  [ $R = \text{tetraphenylporphyrinatozinc(II)}, \text{ZnTPP}$ ;  $p$ -phenyltritylporphyrinatozinc(II),  $\text{ZnTTPP}$ ;  $p$ -phenyltritylporphyrinopalladium(II),  $\text{PdTTPP}$ ] form dyads for through-space triplet energy transfers. The binding constants are on the order of  $20\,000\ \text{M}^{-1}$  in all six cases (298 K). The energy diagram built upon absorption and emission spectra at 298 and 77 K places the  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  and  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  as triplet energy donors, respectively, with respect to the  $\text{ZnTPPCO}_2^-$ ,  $\text{ZnTTPPCO}_2^-$ , and  $\text{PdTTPPCO}_2^-$  pigments, which act as acceptors. Evidence for energy transfer is provided by the transient absorption spectra at 298 K, where triplet–triplet absorption bands of the metalloporphyrin chromophores are depicted at all time (at 298 K) with total absence of the charge-separated state in the nanosecond to microsecond time scale. Rates for energy transfer (ranging in the  $10^4\ \text{s}^{-1}$  time scale) are extracted from the emission lifetimes of the  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  donor in the free chromophore and the host–guest assemblies. The emission intensity of  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  is too weak to measure its spectrum and emission lifetime in the presence of the strongly luminescent metalloporphyrin-containing materials. For the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+} \cdots$  metalloporphyrin dyads, evidence for fluorescence and phosphorescence lifetime quenching of the porphyrin chromophore at 298 K is provided. These quenchings, exhibiting rates of  $10^4$  (triplet) and  $10^8\ \text{s}^{-1}$  (singlet), are attributed to a photoinduced electron transfer from the metalloporphyrin to the cluster due to the low reduction potential.

### Introduction

Through-space singlet energy transfers  $[\text{ET}(\text{S}_1)]$  and energy delocalization and migration (exciton) across the photosynthetic antennas of photosynthetic bacteria, algae, and plants are the two basic nonradiative processes that secure a good constant excitation of the special pair in the reaction center (RC).<sup>1,2</sup> Recently, we investigated both the singlet  $[\text{ET}(\text{S}_1)]$  and triplet  $[\text{ET}(\text{T}_1)]$  energy transfers in cofacial

bisporphyrin dyads (Chart 1), where the donor and acceptor macrocycles are held together by a rigid spacer (except for DPOx, which is flexible). The rigidity of the spacers allows the bismacrocycles to adopt a slipped dimer geometry, keeping the transition moment perfectly parallel. Hence, these

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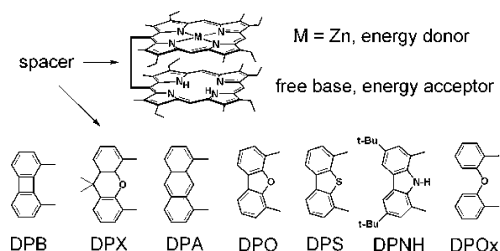
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Chart 1

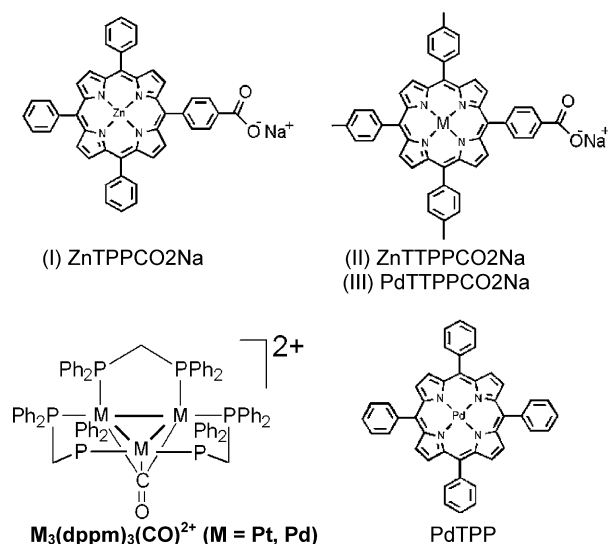


cofacial species can mimic the photophysical behavior of one pair of *bacteriochlorophylls a* located inside the nine apoproteins of the light-harvesting device II (LH II) of the photosynthetic membrane in the purple photosynthetic bacteria.<sup>1</sup>

Whereas ET(S<sub>1</sub>) operates via both Förster (most encountered) and Dexter mechanisms,<sup>6,9</sup> ET(T<sub>1</sub>) usually proceeds via Dexter's mechanism. The latter involves a double electron exchange [LUMO(donor) → LUMO(acceptor) and HOMO(acceptor) → HOMO(donor)], which requires close proximity of the donor and acceptor for better orbital overlap. One of the consequences is that the rate for ET(T<sub>1</sub>),  $k_{ET}(T_1)$ , is slower than that for ET(S<sub>1</sub>). This was demonstrated in a recent literature survey where both  $k_{ET}(S_1)$  and  $k_{ET}(T_1)$  were compared.<sup>10</sup> This paper also showed the relatively low number of data available for  $k_{ET}(T_1)$ .

One of the questions that now arises is, to what extent can through-space ET(T<sub>1</sub>) still operate in electrostatically held dyads in the triplet state because there are no other examples.<sup>10</sup> The separation between an energy donor and acceptor may be variable from one system to another, and so much is still to learn, such as the effect of the separation versus the rate for energy transfer, particularly when the triplet-state energy transfer is known to operate only via a double electron exchange mechanism (i.e., no Förster process). In line with the above comments, we now report a study on through-space ET(T<sub>1</sub>) operating in cluster (donor)<sup>2+</sup>⋯<sup>-</sup>O<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub> (acceptor) dyads across electrostatic bridges composed of unsaturated organometallic clusters of the type M<sub>3</sub>(dppm)<sub>3</sub>(CO)<sup>2+</sup> (M = Pt, Pd; donor) and metallo(II)tetraarylporphyrin carboxylates (acceptor) (Chart 2 and Figure 1). These clusters were chosen because of their structurally well-defined electrostatic ion-pair adducts (the ligand enters the cavity with a 90° angle with respect to the M<sub>3</sub> plane because of steric reasons; Figure 1) and their luminescence properties using these signals as probes for

Chart 2



triplet energy transfer (see the text below and references indicated therein).

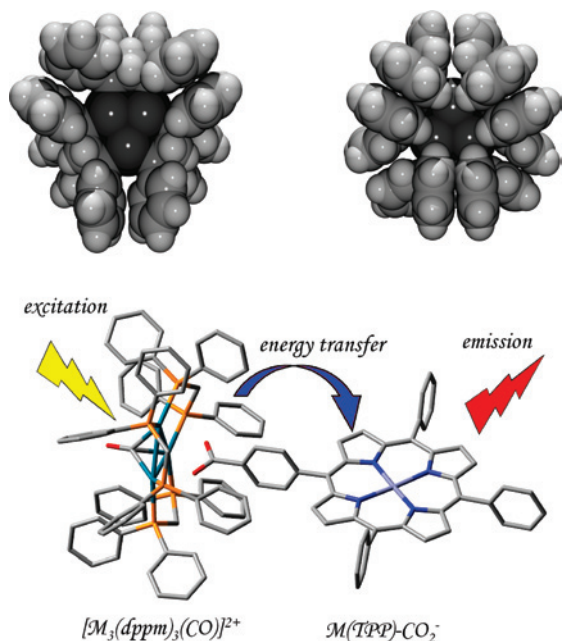
## Experimental Section

**Materials.** The [M<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> clusters (such as PF<sub>6</sub><sup>-</sup> salts) were prepared according to literature procedures.<sup>11</sup> The sodium benzoate was available in our laboratory as (BDH) grade. The 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrinatozinc(II) and 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrinatopalladium(II) and -zinc(II) as well as tetraphenylporphyrinatopalladium(II) (PdTPP) were synthesized according to the literature.<sup>12</sup>

The carboxylate salts [ZnTPPCO<sub>2</sub>Na (I), ZnTTPPCO<sub>2</sub>Na (II), and PdTTPPCO<sub>2</sub>Na (III); Chart 2] were obtained by neutralization of the above corresponding 4-carboxyphenylporphyrin acids. The porphyrin-containing carboxylic acid (0.1 g) was reacted with a large excess (3 g) of sodium carbonate in acetone for 48 h. The reaction mixture was poured into distilled water to dissolve the excess Na<sub>2</sub>CO<sub>3</sub>. The resulting sodium salts were filtered and washed with a slightly alkaline solution (aqueous Na<sub>2</sub>CO<sub>3</sub>, pH ~ 8). The removal of the carboxylic proton was confirmed by <sup>1</sup>H NMR. Data for I. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 7.79–7.81 (m, 9H, phenyl-H<sub>m,p</sub>), 8.05 (d, 2H, COO<sup>-</sup>, COO<sup>-</sup>-phenyl-H<sub>m</sub>, *J* = 7.93 Hz), 8.18 (d, 6H, phenyl-H<sub>o</sub>, *J* = 7.50 Hz), 8.23 (d, 2H, COO<sup>-</sup>, COO<sup>-</sup>-phenyl-H<sub>m</sub>, *J* = 7.79 Hz), 8.76 (m, 8H, β-pyrrole H). Data for II. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 2.67 (s, 9H, tolyl-CH<sub>3</sub>), 7.62 (d, 6H, phenyl-H<sub>m</sub>, *J* = 7.94 Hz), 8.08 (d, 2H, COO<sup>-</sup>, COO<sup>-</sup>-phenyl-H<sub>o</sub>, *J* = 7.93 Hz), 8.20 (d, 2H, COO<sup>-</sup>, COO<sup>-</sup>-phenyl-H<sub>m</sub>, *J* = 7.80 Hz), 8.10 (d, 6H, phenyl-H<sub>o</sub>, *J* = 7.91 Hz), 8.80 (m, 8H, β-pyrrole H). Data for III. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 2.66 (s, 9H, tolyl-CH<sub>3</sub>), 7.62 (d, 6H, phenyl-H<sub>m</sub>, *J* = 7.94 Hz), 8.06 (d, 2H, COO<sup>-</sup>, COO<sup>-</sup>-phenyl-H<sub>o</sub>, *J* = 7.93 Hz), 8.34 (d, 2H, COO<sup>-</sup>, COO<sup>-</sup>-phenyl-H<sub>m</sub>, *J* = 7.93 Hz), 8.48 (d, 6H, phenyl-H<sub>o</sub>, *J* = 8.00 Hz), 8.78 (m, 8H, β-pyrrole H).

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**Figure 1.** Top: Space-filling model of  $[M_3(dppm)_3(CO)]^{2+}$  ( $M = Pd, Pt$ ) showing the cavity above the unsaturated face of the  $M_3$  center. The variable size of the cavity depends on the relative conformation of the dppm ligand. Bottom: Investigated photophysical processes occurring when the  $[M_3(dppm)_3(CO)]^{2+}$  energy donor is anchored with one of the acceptors shown in Chart 2.

**Spectroscopic Measurements.** The spectroscopic and photophysical measurements were carried out in 2MeTHF, which was distilled over calcium hydride under argon. For the  $[Pd_3(dppm)_3(CO)]^{2+}$  cluster, the absorption measurements associated with the binding constant evaluation were carried out in methanol because it was reported to give the largest difference in  $\lambda_{max}$  between the free cluster and host–guest assembly.<sup>13</sup>

**Methodology.** The binding constants ( $K_{11}$ ) were measured according to methodology outlined in ref 13. The typical method used to measure the binding constant was as follows. Two different solutions (**A** and **B**) were prepared in methanol or 2MeTHF. Solution **A** contained the “free cavity” cluster as the  $PF_6^-$  salt ( $[Pd_3(dppm)_3(CO)]^{2+} = 6.70 \times 10^{-5} M$ ,  $[Pt_3(dppm)_3(CO)]^{2+} = 5.85 \times 10^{-5} M$ ). Solution **B** was prepared by mixing of the cluster with exactly the same concentration as that used in solution **A** with an exactly equal concentration of the porphyrin carboxylate salt in order to achieve a 1:1 host–guest assembly. The spectroscopic changes induced by solution **A** as a result of additions of constant volume (0.1 mL) of solution **B** were monitored by measuring the absorption spectra after each addition. The competitive binding constants ( $K_{11}$ ) were measured by plotting  $-1/\Delta A$  vs  $1/[substrate]$  (Benesi–Hildebrand), where  $\Delta A$  is the absorbance change upon an increase in the substrate concentration. The substrate concentration was corrected based on the change of the total volume at each addition, and these adjusted values were used for the plots. The ratio of intercept/slope in this plot gives  $K_{11}$ . As counterchecks, the  $K_{11}$  values were also evaluated by using the Scatchard and Scott plots  $\Delta A/[substrate]$  vs  $-\Delta A$  with  $K_{11} = -\text{slope}$  (Scatchard) and  $-[substrate]/\Delta A$  vs  $[substrate]$  with  $K_{11} = \text{slope}/\text{intercept}$  (Scott) and are all found to be the same within the experimental uncertainties  $\pm 10\%$ . The uncertainties are based on multiple measurements.

**Instruments.** UV–visible spectra were recorded on a Varian Cary 300 spectrophotometer. The emission spectra were obtained

using a double-monochromator Fluorolog 2 instrument from Spex. The emission lifetimes were measured on a TimeMaster model TM-3/2003 apparatus from PTI. The source was a nitrogen laser with a high-resolution dye laser (fwhm  $\sim 1400$  ps), and the fluorescence lifetimes were obtained from deconvolution or distribution lifetime analysis. The uncertainties were about 50–100 ps. The phosphorescence lifetimes were performed on a PTI LS-100 using a 1  $\mu s$  tungsten flash lamp (fwhm  $\sim 1 \mu s$ ). The flash photolysis spectra and the transient lifetimes were measured with a Luzchem spectrometer using the 355 nm line of a YAG laser from Continuum (Serulite) and the 530 nm line from a OPO module pump by the same laser (fwhm = 13 ns).

**Quantum Yields.** Measurements were performed in 2MeTHF at 77 K. Three different measurements (i.e., different solutions) were prepared for each photophysical datum (quantum yields and lifetimes). The sample and standard concentrations were adjusted to obtain an absorbance of 0.05 or less. This absorbance was adjusted to be the same as much as possible for the standard and sample for a measurement. Each absorbance value was measured 10 times for better accuracy in the measurements of the quantum yields. The reference used for quantum yield was TPP(Pd) ( $\Phi = 0.14$ ).<sup>14</sup>

## Results and Discussion

**Absorption Data.** The frontier molecular orbitals (MOs) of the  $M_3(dppm)_3CO^{2+}$  clusters ( $M = Pd, Pt$ ) ( $C_{3v}$  point group) consist of a HOMO ( $a_1$ ) that is mostly composed of M d orbitals with some  $p_z$  and some  $C\equiv O$   $\pi$  and  $\sigma$  characters, forming a weakly Pd–Pd bonding in the  $M_3$  plane and Pd–C antibonding.<sup>15,16</sup> The HOMO–1 consists of degenerate orbitals ( $e$ ), which are almost entirely composed of in-plane M d and p orbitals and are formally M–M bonding. The LUMO ( $a_2$ ) is composed of M in-plane d orbitals ( $d_{xy}, d_{x^2-y^2}$ ) with some minor  $p_x$  and  $p_y$  contributions and some P p components ( $p_y, p_x$ ), forming M–M and M–P antibonding ( $\sigma^*$ ) MOs. The two lowest-energy electronic transitions are the symmetry-forbidden  $a_1 \rightarrow a_2$  and the allowed and polarized  $M_3$  in-plane  $e \rightarrow a_2$  transitions. The latter leads to an intense band, for both  $M = Pd$  and  $Pt$ . The lowest-energy excited states were assigned to  $^1,3[{}^1(a_2)({}^1a_1)]^*$ , which are analogous to the typical  $d_{\sigma}d_{\sigma^*}$  ones for the dinuclear M–M bonded systems.<sup>17</sup>

The  $[Pd_3(dppm)_3(CO)]^{2+}$  cluster in methanol,<sup>15b,18</sup> exhibits a structureless absorption band at  $\sim 494$  nm (i.e.,  $e \rightarrow a_2$ ) at 298 K. In the presence of electron-donor guests, these anions coordinatively add to the unsaturated sites of the  $[Pd_3(dppm)_3(CO)]^{2+}$  cluster inside the cavity [a picture showing the cavity formed by the dppm–phenyl groups is given as Supporting Information (SI)]. This host–guest process is accompanied by spectroscopic changes in the UV–visible spectra with obvious isosbestic points.<sup>18</sup> The

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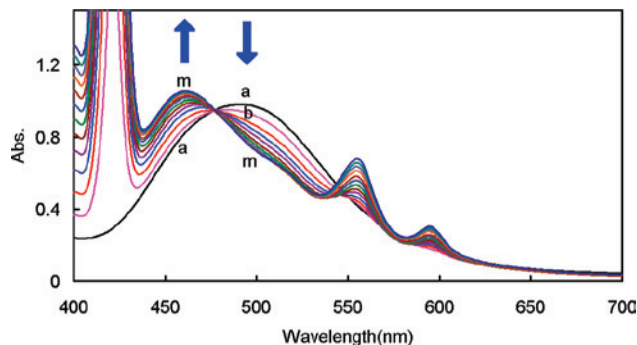
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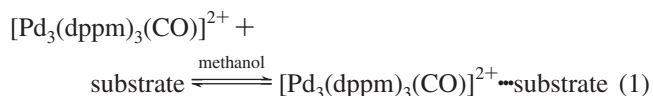
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**Figure 2.** UV–visible spectra for the addition of ZnTPPCO<sub>2</sub>Na (**I**) into a methanol solution of [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>. [[Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>] = 6.70 × 10<sup>−5</sup> M (curve a); [I] = 0.42 × 10<sup>−5</sup> M (curve b). Curves c–m were obtained with successive additions of 0.67 × 10<sup>−5</sup> M of **I**. (The arrows indicate the direction of absorption change with the addition of guests.)

binding constant,  $K_{11}$ , of a substrate inside the cavity is related to the charge, electron-donating ability, size, and hydrophobic properties of the substrates, which is consistent with the bifunctional recognition properties of the cluster cavity (cationic metal center and hydrophobic pocket).<sup>13</sup>  $\lambda_{\max}$  of absorption of this intense lowest-energy band ( $e \rightarrow a_2$ ) of the [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> cluster (such as the PF<sub>6</sub><sup>−</sup> salt) blue-shifts from 494 to about 466 nm (the exact position depends on the substrate), in the absence and presence of a guest molecule, respectively.<sup>15</sup>

The spectroscopic changes in the absorption spectra upon successive additions of three carboxylate-containing porphyrin solutions at constant concentration (**I–III**, Chart 1) to a [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)](PF<sub>6</sub>)<sub>2</sub> solution (6.70 × 10<sup>−5</sup> M) in methanol at 298 K are now presented. The presence of isosbestic points in the evolution of the UV–visible spectra indicating a 1:1 equilibrium between the free cluster (empty cavity) and host–guest assemblies is depicted (eq 1).



where substrate = **I–III**. The spectroscopic changes accompanying the successive addition of ZnTPPCO<sub>2</sub>Na (**I**) to a solution of [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)](PF<sub>6</sub>)<sub>2</sub> are shown in Figure 2 as an example. The addition of ZnTPPCO<sub>2</sub>Na (**I**), while keeping the concentration of [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> constant, induces a decrease of the absorption at  $\lambda_{\max}$  of 492 nm (free cavity) and an increase of a new band at  $\lambda_{\max}$  of 460 nm (filled cavity).

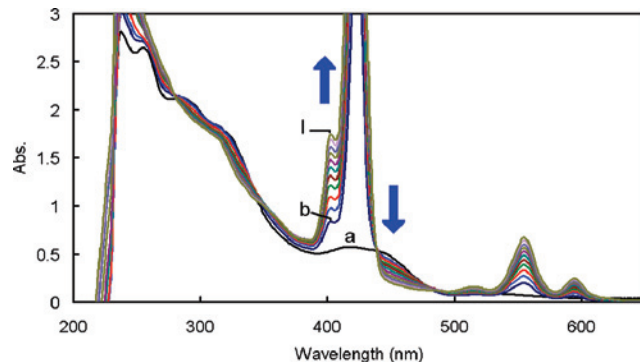
The formation of 1:1 host–guest complex (here **I**⋯[Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>) was further demonstrated by examining the Benesi–Hildebrand, Scatchard, and Scott plots.<sup>16,19</sup> These plots exhibit straight lines with concentrations of guests constants varying from 0.42 to 2.84 × 10<sup>−5</sup> M (see the SI). The extracted  $K_{11}$  values (Table 1) using the three methods, are almost the same, which is consistent with the 1:1 complex formation.

Very similar results are obtained for ZnTTPPCO<sub>2</sub><sup>−</sup> and PdTTPPCO<sub>2</sub><sup>−</sup> with [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> (see the SI). The

**Table 1.**  $K_{11}$  Values for **I–III** with [Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> in MeOH at 298 K<sup>a</sup>

substrate	$K_{11}$ (M <sup>−1</sup> )		
	Benesi–Hildebrand	Scott	Scatchard
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	22 500	19 300	19 000
ZnTTPPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	18 900	17 100	20 300
PdTTPPCO <sub>2</sub> <sup>−</sup> ( <b>III</b> )	20 100	18 500	20 200

<sup>a</sup> The uncertainties are ±10% based on multiple measurements.



**Figure 3.** UV–visible spectra for the addition of ZnTPPCO<sub>2</sub>Na (**I**) into a 2MeTHF solution of [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>. [[Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>] = 5.85 × 10<sup>−5</sup> M (curve a); [I] = 0.79 × 10<sup>−5</sup> M (curve b). Curves c–l were obtained with successive additions of 0.67 × 10<sup>−5</sup> M of **I**. (The arrows indicate the direction of absorption change with the addition of guests.)

same  $K_{11}$  constants are also found for all three complexes (**I**⋯[Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>, **II**⋯[Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>, and **III**⋯[Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>), which is consistent with the nature of the electrostatic interactions (Pd<sub>3</sub><sup>2+</sup>⋯O<sub>2</sub>C–R) as well as the steric hindrance being the same for all three cases.

The observed  $K_{11}$  values are higher (by a factor of ~2) than that reported for the sodium benzoate⋯[Pd<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> complex (10 000 M<sup>−1</sup>).<sup>13</sup> We tentatively explain this difference by a contribution of the high electron density of porphyrin inducing a high electron density at the carboxylate center. This increase would result in stronger interactions with a divalent cluster cation and hence increasing binding constants. This hypothesis is based on our previous studies on various RCO<sub>2</sub><sup>−</sup> substrates where R was varied (Me, Ph, etc.).<sup>13</sup>

The [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> cluster behaves similarly. The addition of solutions containing the porphyrin anions into the cluster-containing solution resulted in the formation of a 1:1 complex as evidenced by the spectral changes, isosbestic points, and data analysis. Indeed, spectroscopic changes in the UV–visible spectra of a [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> solution upon the addition of ZnTPPCO<sub>2</sub>Na (**I**) are noticed (Figure 3). Despite the strong overlap between the  $a_2 \rightarrow e$  band of the cluster and the Soret absorption of the porphyrin chromophore, monitoring is possible. The decrease of the shoulder absorption located at 445 nm (free [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>) was monitored (Figure 3), hence extracting the binding constant. The band associated with the host–guest complex, which is expected to be blue-shifted in comparison with the free cluster, is hidden under the strong Soret band of ~420 nm.

The  $K_{11}$  values for the ZnTPPCO<sub>2</sub><sup>−</sup> (**I**)⋯[Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> pair were also extracted from the Benesi–Hildebrand, Scatchard, and Scott plots (Table 2). Again, the plots (see

(19) Connors, K. A. *Binding Constants: The Measurements of Molecular Complex Stability*; John Wiley & Sons: New York, 1987.

**Table 2.**  $K_{11}$  Values for **I–III** with  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  in 2MeTHF at 298 K<sup>a</sup>

substrate	$K_{11}$ ( $\text{M}^{-1}$ )		
	Benesi-Hildebrand	Scott	Scatchard
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	21 900	25 500	19 900
ZnTTPPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	19 600	20 500	19 300
PdTTPPCO <sub>2</sub> <sup>−</sup> ( <b>III</b> )	17 100	18 300	18 400

<sup>a</sup> The uncertainties are  $\pm 10\%$  based on multiple measurements.

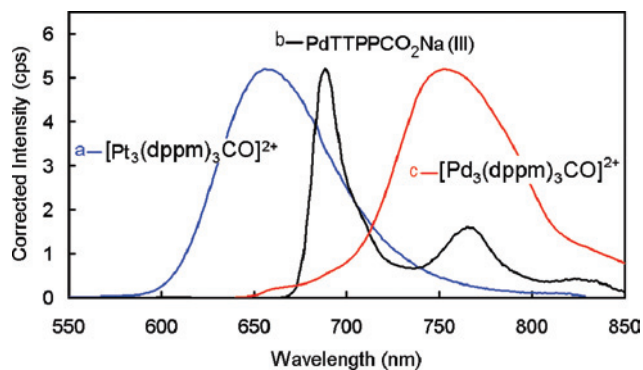
the SI) exhibit straight lines consistent with the formation of a 1:1 complex formation.<sup>16,19</sup> Moreover, the binding constants were also almost the same in all three methods.

The  $K_{11}$  values for all three cases of metalloporphyrin-containing substrates are very similar to those obtained for the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  pairs. All in all, the close similarity in  $K_{11}$  values reinforced that the interactions are driven by electrostatic interactions.

In order to secure this conclusion, control experiments were performed. Sodium benzoate and PdTPP (Chart 2) were placed in the presence of  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ . The spectrum recorded for the sodium benzoate– $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  system (see Figures SI.12–SI.15 in the SI) exhibit isosbestic points as expected, consistent with the formation of a host–guest complex.<sup>18</sup> The spectral changes are difficult to observe, where a shift of only  $\sim 2$  nm is observed between the free  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  ( $\lambda_{\text{max}} = 417$  nm) and the host–guest complex ( $\lambda_{\text{max}} = 415$  nm) (see Figures SI.12 and SI.13 in the SI). The calculated  $K_{11}$  value ( $10\ 100\ \text{M}^{-1}$ ) using the same methodologies (Benesi-Hildebrand, Scatchard, and Scott) agrees with the value reported for the case of sodium benzoate– $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ ,  $10\ 000\ \text{M}^{-1}$ .<sup>13</sup> Moreover, the addition of PdTPP to  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  and  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  solutions did not lead to spectral changes (i.e., blue-shift of the  $a_2 \rightarrow e$  band), except for linear mathematical additions of the intensity of the added component, or to the formation of any isosbestic points (see Figures SI.14 and SI.15 in the SI). Examination of the spectroscopic changes in the cases of both sodium benzoate and PdTPP clearly demonstrates that the spectral changes observed in the absorption spectra of  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  and  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  are due to the interactions between the negatively charged carboxylate anion and the positive charge of the cluster. The size of the  $K_{11}$  data ( $\sim 20\ 000\ \text{M}^{-1}$ ) indicates that the interactions are strong but reversible.<sup>19</sup>

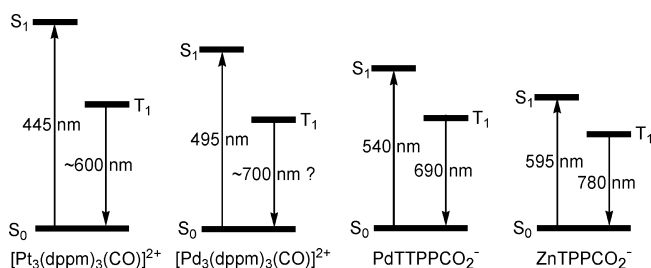
**Photophysical Measurements.** Previous work from our group illustrated that the host–guest interactions are still present in the excited states of the  $[\text{M}_3(\text{dppm})_3(\text{CO})]^{2+}$  clusters ( $\text{M} = \text{Pd}, \text{Pt}$ ).<sup>15,20</sup> Interestingly, the cluster cavity in the excited state is still hydrophobic but exhibits a larger size. Indeed, the cavity size in the ground state has a diameter of about 3–4 Å, whereas in the excited state, the antibonding nature of the LUMO makes the M–M and M–P bond distances longer than that of the ground state, which will result in increased cavity sizes. The hydrophobic nature and increased cavity size for the excited state would intuitively achieve better substrate–cluster interactions.

The clusters exhibit emission bands at 755 and 655 nm for  $\text{M} = \text{Pd}$  and  $\text{Pt}$ , respectively, at 77 K (Figure 4) but are



**Figure 4.** Emission of (a)  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  alone (as the  $\text{PF}_6^-$  salt),  $\lambda_{\text{ex}} = 450$  nm, (b) **III**,  $\lambda_{\text{ex}} = 515$  nm, and (c)  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  (as the  $\text{PF}_6^-$  salt),  $\lambda_{\text{ex}} = 450$  nm, in 2MeTHF at 77 K. The emission intensities were adjusted to fit in the frame. The emission band for  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  is, in fact, very weak (by at least 2 orders of magnitude). Smoothing was applied in this case.

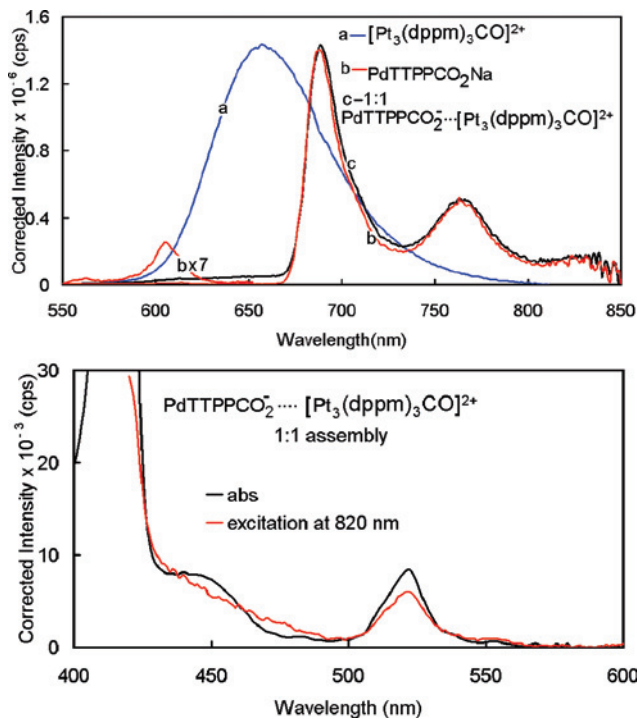
#### Scheme 1



optically silent at 298 K. The photophysical measurements on the 1:1 host–guest complexes described above between ZnTTPPCO<sub>2</sub>Na (**I**), ZnTTPPCO<sub>2</sub>Na (**II**), and PdTTPPCO<sub>2</sub>Na (**III**) and the  $[\text{M}_3(\text{dppm})_3(\text{CO})]^{2+}$  clusters ( $\text{M} = \text{Pd}, \text{Pt}$ ) were carried out in 2MeTHF at both 77 and 298 K because **I–III** are emissive in both conditions.

The 0–0 phosphorescence peak for **III** in 2MeTHF (for example) is observed at 690 nm at 77 K, whereas the 0–0 peaks for **I** and **II** are found at 780 nm (see Figures SI.16 and SI.17 in the SI). The exact position of the 0–0 peak of the clusters is not known; one can approximate their position by determining the position where the emission starts appearing on the high-energy side ( $\sim 600$  and  $\sim 700$  nm for  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  and  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ , respectively; Figure 4). The energy gap between these two latter values ( $2380\ \text{cm}^{-1}$ ) appears reasonable in comparison with the energy gap measured at the maximum of the absorption bands of the two clusters (445 and 495 nm, respectively;  $2270\ \text{cm}^{-1}$ ). Using these values, an energy diagram can be constructed (Scheme 1) and allows to predict that both clusters and the metalloporphyrins should act as energy donors and acceptors, respectively.

The only uncertainty is the relationship between the triplet state of  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  and **III** (Figure 4). Experimental evidence provided below demonstrates that the cluster is also the donor in this pair. Moreover, in the presence of acetate and benzoate, the emission maximum of  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  blue-shifts (modestly) by about  $260\ \text{cm}^{-1}$  (see the SI), whereas the emission band for  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  remains little affected in the presence of the same substrates. All in all, the predicted role of the clusters as energy donors

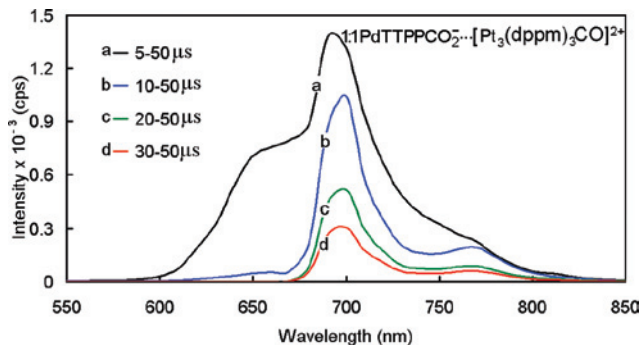


**Figure 5.** Top: Emission spectra of (a)  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ , (b)  $\text{III}$ , (c) 1:1  $\text{III} \cdots [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  in 2MeTHF at 77 K excited at 450 nm.  $[\text{PdTTPPCO}_2^-] = [[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}] = 6 \times 10^{-5}$  M in all cases. Bottom: Comparison of the absorption (black) and excitation (red) spectra of the  $\text{PdTTPPCO}_2^- \cdots [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  assembly at 77 K in 2MeTHF, monitored at 820 nm.

remains, as well as the uncertainty between  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  and  $\text{III}$ .

**Host–Guest Interactions with  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  (Luminescence Spectra).** A typical experiment where the emission spectra of the cluster, the metalloporphyrin unit, and the 1:1 host–guest assembly are compared is shown in Figure 5. The other two anionic metalloporphyrins, **I** and **II**, behave the same way, and the corresponding experiments are provided in the SI. No significant spectroscopic changes were observed for the emission bands of the free metalloporphyrin carboxylate anions compared to the 1:1 assembly with  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ . In all cases [Figures 5 (top) and SI.16 and SI.17 in the SI], both the free base porphyrin and the 1:1 assembly showed a weak band at  $\sim 605$  nm assigned to a  $\pi\pi^*$  fluorescence of the metalloporphyrin chromophore. The signal is expectedly weak because of the heavy-atom effect induced by the Pd metal. Long-lived and intense emission bands are observed in the range of 650–850 nm and are assigned to be the  $\pi\pi^*$  phosphorescence of the metalloporphyrin chromophore.<sup>14,21</sup>

No spectroscopic changes in the band shape and intensity (keeping the concentrations the same) are observed for the metalloporphyrin emission in the 1:1 complexes. On the other hand, the 650 nm emission intensity of  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$



**Figure 6.** Time-resolved emission spectra for 1:1  $\text{III} \cdots [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  assembly in 2MeTHF at 77 K excited at 450 nm.  $[\text{PdTTPPCO}_2^-] = [[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}] = 6 \times 10^{-5}$  M. Time windows: 5–50, 10–50, 20–50, and 30–50  $\mu\text{s}$  for a, b, c, and d, respectively.

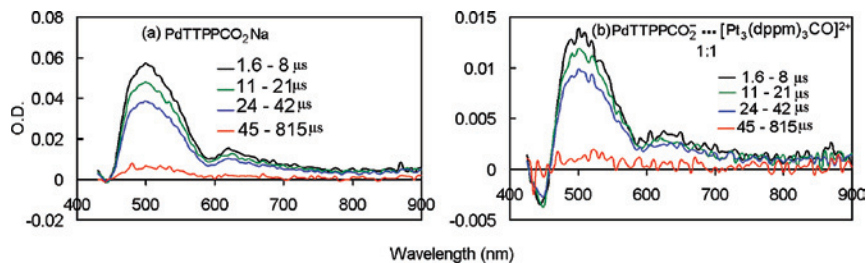
is largely decreased in the 1:1 mixture where a weak shoulder at  $\sim 650$  nm (i.e., emission of the  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster) is barely noticeable. The two other complexes (with **I** and **II**) are provided in the SI (see Figures SI.16 and SI.17). The corresponding spectra recorded at 298 K exhibit a similar behavior, and the spectra are also given in the SI (see Figures SI.18–SI.20). The excitation spectra of  $\text{III} \cdots [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  at 77 K in 2MeTHF monitored at 820 nm, where the cluster emission is no longer apparent but the phosphorescence of the metalloporphyrin is still observable, exhibit all of the absorption features belonging to both chromophores (Figure 5, bottom). This result indicates that the observation of metallophosphorescence arises from both the macrocycle itself and the cluster, meaning that triplet energy transfer from the cluster to the metalloporphyrin takes place. The two other  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ -containing assemblies (**I** and **II**) exhibit the same behavior (see Figures SI.31 and SI.32 in the SI).

The time-resolved spectra in the microsecond time scale for the 1:1  $\text{PdTTPPCO}_2^- / [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  mixture (Figure 6) exhibit emissions from both the cluster and the porphyrin chromophore. Both emissions are readily observed, but the 650 nm band (due to the cluster emission) relaxes more quickly than that for the porphyrin macrocycle. In comparison with the free  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ , the cluster emission in the host–guest assembly decays faster, whereas the metalloporphyrin chromophore exhibits the same rate of decay. These observations support the presence of a triplet energy transfer from  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  to the  $\text{PdTTPPCO}_2^-$  unit in the assembly.

The two other assemblies (with **I** and **II**) behave the same way (see Figures SI.21 and SI.22 in the SI), where the 650 nm (cluster emission) signal decreases faster than of the 700 and 800 nm phosphorescence signals of the two other metalloporphyrins.

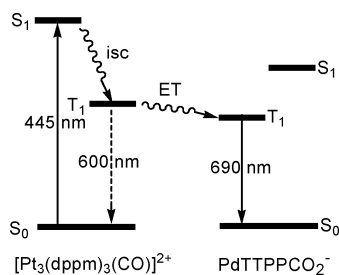
**Transient Absorption.** The recorded transient absorption spectra of  $\text{PdTTPPCO}_2\text{Na}$  (i.e., triplet–triplet absorption) and a 1:1  $\text{III} / [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  mixture in 2MeTHF at 298 K (Figure 7) exhibit a broad signal centered at  $\sim 500$  nm. The two signals are essentially the same, but the transient absorption undergoes some blue shift ( $\sim 5$  nm) resembling the effect of the host–guest behavior on the absorption spectra. The blue shift is most likely due to host–guest interactions.

(21) (a) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407–2411. (b) Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1281–1291. (c) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771–11782. (d) Sessler, J. L.; Jayawickramarajah, J.; Gouloumis, A.; Torres, T.; Guldi, D.; Maldonado, S.; Stevenson, K. *J. Chem. Commun.* **2005**, 1892–1894.



**Figure 7.** Transient absorption spectra of (a) **III** and (b) 1:1 PdTTPPCO<sub>2</sub><sup>-</sup> ··· [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>. [PdTTPPCO<sub>2</sub><sup>-</sup>] = [[Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>] = 6 × 10<sup>-5</sup> M, in 2MeTHF at 298 K. (Spectra were measured at different delay times and λ<sub>exc</sub> = 355 nm.)

### Scheme 2



This 500 nm band for the uncomplexed porphyrin is due to triplet–triplet absorption. Because the band shape is the same in the assembly and in the free metalloporphyrin, the signal is confidently assigned to triplet–triplet absorption as well.

The reported triplet–triplet absorption for zinc tetraphenylporphyrin (ZnTPP) exhibits transient bands at 470 nm and that for PdTPP at 450 nm, agreeing with the assignment.<sup>21</sup> On the other hand, a very broad transient absorption band in the 600–1100 nm region is reported for the corresponding radical cation.<sup>21</sup> However, because of the very large signal generally seen for the radical cation, it would not be reasonable to totally preclude its existence. However, because the fluorescence and phosphorescence lifetimes for three metalloporphyrin remain the same in the uncomplexed species and in the assemblies (see below), no quenching by electron transfer of these species occurs. The recorded spectra given in Figure 7 compare favorably to those previously reported for metalloporphyrins while showing clear differences with the reported spectra of the porphyrin radical cation. All in all, this means that there is no or a very slow electron-transfer process occurring (knowing that the charge-separated state would generate species absorbing at a different place and with a different band shape). Scheme 2 shows the energy diagram for the [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> ··· PdTTPPCO<sub>2</sub><sup>-</sup> assembly (as an example) describing the energy transfer. The transient absorption data are available in Table 3.

The transient absorption was measured in the presence and absence of O<sub>2</sub>, and the obtained spectra are given in the SI (Figures SI.23–SI.27). The transient lifetime was measured in the absence and presence of O<sub>2</sub>, and the obtained lifetimes are listed in Table 3. The observed decrease in the lifetime clearly supports the interpretation of the obtained signal to the transient porphyrin triplet state.

**Table 3.** Transient (Triplet–Triplet) Absorption Lifetimes of the Metalloporphyrin Species in the Free Molecules and 1:1 Host–Guest [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> ··· O<sub>2</sub>CR Assemblies Measured in 2MeTHF at 298 K in the Presence and Absence of O<sub>2</sub><sup>a</sup>

substrate	τ (μs)			
	substrate alone		1:1 [Pt <sub>3</sub> (dppm) <sub>3</sub> (CO)] <sup>2+</sup> ··· substrate	
	without O <sub>2</sub>	in the presence of O <sub>2</sub> (air)	without O <sub>2</sub>	in the presence of O <sub>2</sub> (air)
ZnTTPPCO <sub>2</sub> <sup>-</sup> ( <b>I</b> )	145	5	148	6
ZnTTPPCO <sub>2</sub> <sup>-</sup> ( <b>II</b> )	137	4	141	5
PdTTPPCO <sub>2</sub> <sup>-</sup> ( <b>III</b> )	220	2	227	3

<sup>a</sup> The uncertainties are ±7% based on multiple measurements.

**Table 4.** Emission Lifetimes of [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> and Its 1:1 Assemblies in 2MeTHF at 77 K (λ<sub>em</sub> = 640 nm)<sup>a</sup>

	τ <sub>e</sub> (μs)	k <sub>ET</sub> (s <sup>-1</sup> )
[Pt <sub>3</sub> (dppm) <sub>3</sub> (CO)] <sup>2+</sup> <sup>b</sup>	12.63 ± 0.07	
[Pt <sub>3</sub> (dppm) <sub>3</sub> (CO)] <sup>2+</sup> ··· PhCO <sub>2</sub> <sup>-</sup> (Na <sup>+</sup> salt)	12.40 ± 0.05	no transfer
[Pt <sub>3</sub> (dppm) <sub>3</sub> (CO)] <sup>2+</sup> ··· ZnTPPCO <sub>2</sub> <sup>-</sup>	9.57 ± 0.04	2.4 × 10 <sup>4</sup>
[Pt <sub>3</sub> (dppm) <sub>3</sub> (CO)] <sup>2+</sup> ··· ZnTTPPCO <sub>2</sub> <sup>-</sup>	10.30 ± 0.03	2.1 × 10 <sup>4</sup>
[Pt <sub>3</sub> (dppm) <sub>3</sub> (CO)] <sup>2+</sup> ··· PdTTPPCO <sub>2</sub> <sup>-</sup>	11.80 ± 0.08	0.6 × 10 <sup>4</sup>

<sup>a</sup> All of the emission decay traces are monoexponential. <sup>b</sup> Φ<sub>P</sub> for this compound was found to be 0.073 ± 10%.

No triplet–triplet absorption spectra were observed for [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> alone, presumably because its triplet lifetime was too short at 298 K (i.e., <13 ns).

**Emission Lifetime and Energy Transfers.** The change in emission lifetimes of the [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> cluster upon the addition of porphyrin substrates as well as that of the free metalloporphyrins and their corresponding 1:1 assemblies with [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> are listed in Tables 4 and 5.

The emission lifetimes for [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> and the [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> ··· O<sub>2</sub>CPh assembly in 2MeTHF at 77 K are practically identical (Table 4), consistent with the absence of triplet energy transfer. On the other hand, the emission lifetimes of the [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup> ··· **I**, ··· **II**, and ··· **III** assemblies are shorter than that for the cluster alone, indicating obvious interactions from the Pt<sub>3</sub> center to the metalloporphyrin chromophore. The decrease in the emission lifetime is due to triplet energy transfer, and the k<sub>ET</sub> values are extracted from eq 2:<sup>10</sup>

$$k_{\text{ET}} = \left( \frac{1}{\tau_{\text{e}}} - \frac{1}{\tau_{\text{e}}^0} \right) \quad (2)$$

where τ<sub>e</sub><sup>0</sup> is the emission lifetime for the free donor (i.e., [Pt<sub>3</sub>(dppm)<sub>3</sub>(CO)]<sup>2+</sup>) where no energy transfer takes place and τ<sub>e</sub> is the emission lifetime of the donor in the dyad (the

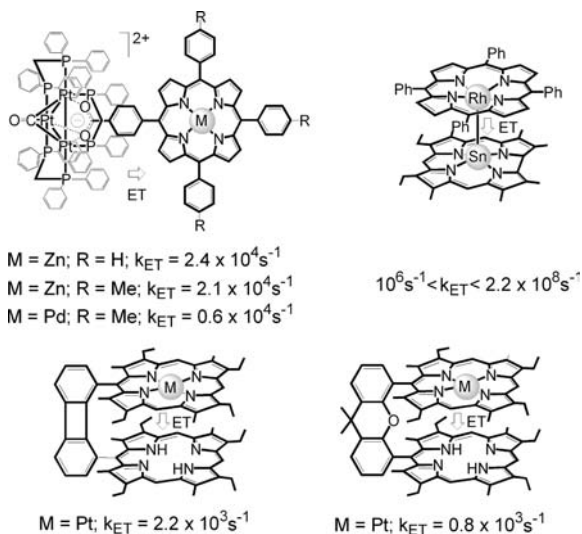
**Table 5.** Photophysical Data for the Free Metalloporphyrins **I–III** and Their 1:1 Host–Guest Complexes with  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ 

substrate in 2MeTHF at 77 K	substrate alone				1:1 $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ •••substrate			
	$\Phi^b$ (520 nm) <sup>c</sup>		$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ (ms) ( $\lambda_{\text{max}}^d$ )	$\Phi^b$ (520 nm) <sup>c</sup>		$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ (ms) ( $\lambda_{\text{max}}^d$ )
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	0.039	0.013	2.73 ± 0.02 (600) <sup>d</sup>	25.95 ± 0.28 (780) <sup>d</sup>	0.039	0.013	2.70 ± 0.02 (600) <sup>d</sup>	26.20 ± 2.72 (780) <sup>d</sup>
ZnTTTPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	0.036	0.002	2.52 ± 0.24 (600) <sup>d</sup>	19.40 ± 0.40 (780) <sup>d</sup>	0.039	0.003	2.53 ± 0.08 (600) <sup>d</sup>	15.20 ± 1.20 (780) <sup>d</sup>
PdTTTPCO <sub>2</sub> <sup>−</sup> ( <b>III</b> )	>0.001	0.124	0.11 ± 0.03 (605) <sup>d</sup>	1.54 ± 0.05 (690) <sup>d</sup>	>0.001	0.120	0.13 ± 0.02 (605) <sup>d</sup>	1.56 ± 0.05 (690) <sup>d</sup>

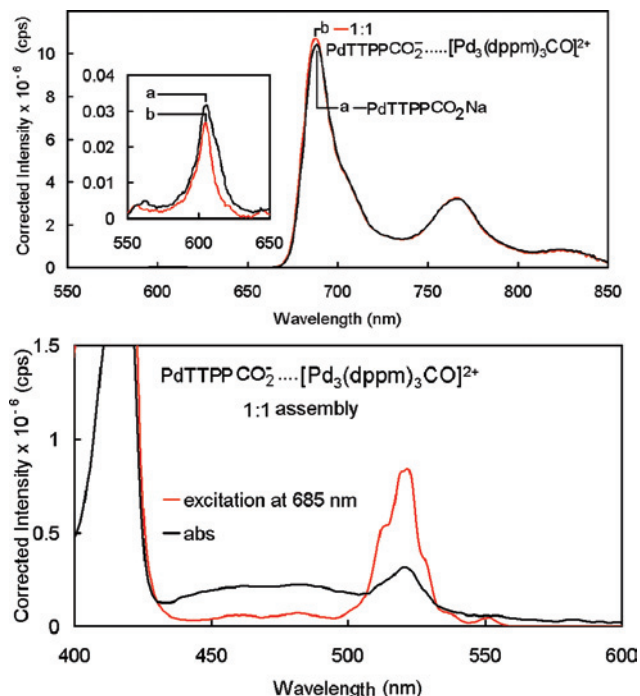
substrate in 2MeTHF at 298 K	substrate alone		1:1 $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ •••substrate	
	$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ (μs) ( $\lambda_{\text{max}}^d$ )	$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ (μs) ( $\lambda_{\text{max}}^d$ )
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	0.63 ± 0.03 (605) <sup>d</sup>	<i>e</i>	0.65 ± 0.03 (605) <sup>d</sup>	<i>e</i>
ZnTTTPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	0.38 ± 0.04 (605) <sup>d</sup>	<i>e</i>	0.33 ± 0.03 (605) <sup>d</sup>	<i>e</i>
PdTTTPCO <sub>2</sub> <sup>−</sup> ( <b>III</b> )	<i>e</i>	277 ± 14 (700) <sup>d</sup>	<i>e</i>	295 ± 1.85 (700) <sup>d</sup>

<sup>a</sup> All of the emission decay traces are monoexponential. <sup>b</sup>  $\Phi_F$  and  $\Phi_P$  are reported at ±10% of uncertainties. <sup>c</sup> Excitation wavelength. <sup>d</sup> The values in parentheses are the wavelengths where the lifetimes were measured. <sup>e</sup> The intensity is too weak to be measured.

**Scheme 3**

1:1 assemblies). The  $k_{\text{ET}}$  values are in the  $10^4 \text{ s}^{-1}$  range (Table 4), which can be described as being on the slow side in comparison with other assemblies of polyporphyrins.<sup>10</sup> This is consistent with the through-space process where orbital overlaps are more difficult. A comparison with other cofacial systems, where through-space triplet energy transfer also take place,<sup>7,8</sup> is made in Scheme 3.

The electrostatic assemblies reported here are about 1 order of magnitude larger than the cofacial systems. The average Pd•••O distance between the related assemblies  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ ••• $-\text{O}_2\text{CCF}_3$  is  $\sim 2.7 \text{ \AA}$ .<sup>13</sup> Assuming that this distance is transferable to the assemblies studied here (because the Pd and Pt atoms exhibit about the same covalent and van der Waals radii), the anticipated donor–acceptor separations in these dyads are shorter than that found for  $C_{\text{meso}} \cdots C_{\text{meso}}$  of the diphenylene (3.80 Å) and the xanthen spacer systems (4.32 Å),<sup>6</sup> and so they predict slower rates (as observed).<sup>10</sup> The comparison is crude because the  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ ••• $-\text{O}_2\text{CR}$  assemblies are not cofacial, but the observed rates are still considered logical with the amplitude of the donor–acceptor separations. The through-bond process is generally found to be faster than the through-space one.<sup>10</sup> Scheme 3 shows a related example containing a cofacial dyad held by a Rh–Sn single bond ( $\sim 2.6 \text{ \AA}$ ). The observed rates range between  $10^6$  and  $2.2 \times 10^8 \text{ s}^{-1}$ ,<sup>7</sup> much



**Figure 8.** Top: Phosphorescence spectra of (a) **III** and (b) 1:1 **III**••• $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  in 2MeTHF at 77 K excited at 515 nm. At this wavelength, both the cluster and the porphyrin chromophores are excited (see Figure 1).  $[\text{PdTTTPCO}_2^-] = [[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}] = 2 \times 10^{-5} \text{ M}$ . Insert: identical but this is the fluorescence. The spectra are adjusted so that their intensities would match. There is no evidence for  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  emission because it is weak in comparison with the metalloporphyrin. Bottom: Comparison of the absorption (black) and excitation (red) spectra of the  $\text{PdTTTPCO}_2^-$ ••• $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  assembly at 77 K in 2MeTHF, monitored at 685 nm.

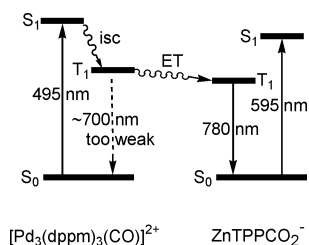
faster than others operating via a through-space mechanism. The rates in the cluster assemblies make sense.

**Interactions with  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  (Luminescence Spectra).**  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  is predicted to be a triplet energy donor with respect to both **I** and **II** (Scheme 1). In the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ ••• $\text{PdTTTPCO}_2\text{Na}$  case, this is uncertain from the Figure 4 only. Evidence that this cluster also acts as a triplet energy donor is provided below.

The emission spectra of  $\text{PdTTTPCO}_2\text{Na}$  (as an example) and its corresponding 1:1 assembly with  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  in 2MeTHF at 77 K are shown in Figure 8. The other two anionic porphyrins (**I** and **II**) behave the same way and are placed in the SI (see Figures SI.24 and SI.25). Both the uncomplexed metalloporphyrin and the 1:1 aggregates show



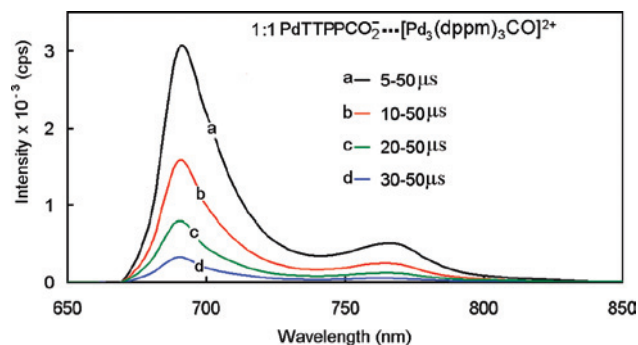
## Scheme 4



the expected band at  $\sim 605$  nm, associated with a weak  $\pi\pi^*$  fluorescence for the  $\text{PdTPPPCO}_2^-$  chromophore and a long-lived porphyrin-localized  $\pi\pi^*$  phosphorescence in the 650–850 nm range.<sup>14,21</sup> No significant changes are observed in the emissions band shape of the free porphyrin chromophore compared to the 1:1 assembly, except that we find that the emission intensity is lower in the assembly.

One major difference is, however, noted for three possible assemblies with the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster. The excitation spectra do superpose the absorption ones perfectly, particularly for the band due to the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster, which appears to be almost totally absent from the excitation spectra. We used two different emission wavelengths at 650 and 820 nm. These wavelengths were selected because they are situated on the high- and low-energy sides of the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster emission, respectively, and within the fluorescence and phosphorescence bands of the metalloporphyrins and for comparison purposes. Because the phosphorescence intensity of the Zn-containing chromophores is weak, the measurements of the excitation spectra monitored at 820 nm lead to lesser quality spectra even using multiscans. Nonetheless, the absence (or the weakness) of the excitation signal associated with the cluster component indicates that excitation in the cluster band does not contribute efficiently to the metalloporphyrin emission in the dyad complexes. Hence, this result demonstrates the absence of efficient triplet energy transfers. For a demonstration that energy transfer is still operating, the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+} \cdots \text{PdTPPPCO}_2^-$  assembly was investigated using 685 nm as monitoring wavelength where the phosphorescence is very intense (but not the cluster), hence improving the quality of the signal. Indeed, two weak features between 450 and 500 nm attributable to the cluster are observed (Figure 8) in the excitation spectra of this assembly. Again the intensity is weak, meaning that the transfer is not efficient but is clearly present (Scheme 4). So, the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster and  $\text{PdTPPPCO}_2^- \cdots$  act as a triplet energy donor and acceptor, respectively. On the basis of this conclusion, one can also reasonably state that triplet energy transfer in the two other  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster assemblies must also occur (Scheme 4).

The emission spectra at 298 K behave the same way as those at 77 K and are placed in the SI (see Figures SI.26–SI.28). The emission band located at  $\sim 750$  nm for the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster is not observed because of its relatively very weak intensity. In an attempt to discriminate this band from the assembly, time-resolved spectra for the  $\text{PdTPPPCO}_2^- \cdots [\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  assembly were studied (Figure 9). Despite several attempts, the search was



**Figure 9.** Time-resolved emission spectra of the 1:1  $\text{PdTPPPCO}_2^- \cdots [\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  assembly in 2MeTHF at 77 K excited at 450 nm.  $[\text{PdTPPPCO}_2^-] = [[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}] = 6 \times 10^{-5}$  M. Time windows: 5–50, 10–50, 20–50, and 30–50  $\mu\text{s}$  for a, b, c, and d, respectively.

unfruitful, suggesting that emission is far too weak and short-lived to be found in comparison with the much stronger phosphorescence signal of the metalloporphyrin chromophores or is totally quenched.

The  $\tau_F$  values of the metalloporphyrin chromophores at 77 K remain, at first glance, little affected in the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+} \cdots \text{O}_2\text{CR}$  assemblies (Table 6), but in absolute value (i.e., excluding the uncertainties), a small decrease is noted, meaning quenching. Similarly, the phosphorescence lifetimes decrease by a factor of 2–3 in the host–guest assemblies, contrasting with the  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+} \cdots \text{O}_2\text{CR}$  systems (**I–III**).

A comparison of the data in Tables 5 and 6 shows clearly the trend. If we consider these changes in  $\tau_P$  values as a quenching process of the metalloporphyrin chromophore by the cluster, then quenching rates ( $k_Q$ ) extracted the same way as in eq 2 ( $k_{ET}$  is replaced by  $k_Q$ ) are found to be on the order of  $10^1$ – $10^2$   $\text{s}^{-1}$  for all three cases. These values are clearly slow. An element for the assignment for this slow quenching, which is absent in the  $\text{Pt}_3$ -containing cluster assemblies, is found in the 298 K data. Indeed, the  $\tau_P$  value of  $\text{PdTPPPCO}_2^-$  in 2MeTHF at 298 K on going from the uncomplexed compound  $\text{PdTPPPCO}_2^-$  to the electrostatic dyad  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+} \cdots \text{O}_2\text{CPdTPPP}$  also decreases, but  $k_Q$  is on the order of  $0.70 \times 10^4$   $\text{s}^{-1}$ , which is slow but faster than that measured at 77 K. This key information (i.e.,  $k_Q$  faster at 298 K with respect to  $k_Q$  at 77 K) allows one to suspect that an electron-transfer process going from the metalloporphyrin center to the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster takes place.

**Transient Absorption.** The transient spectra of the metalloporphyrins exhibit the same transient triplet–triplet absorption band (see **III** and its 1:1 host–guest complex with  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  in 2MeTHF at 298 K in Figure 10), meaning that despite quenching some residual species are still present. The corresponding transient spectra for **I** and **II** in the presence and absence of  $\text{O}_2$  are available in the SI (see Figures SI.33–SI.37). The triplet–triplet spectra for the studied porphyrins and their 1:1 host–guest assemblies with  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  are almost the same and superpose that reported for the other porphyrins<sup>21</sup> and that presented in Figure 7 for the  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+} \cdots \text{I}$ ,  $\cdots \text{II}$ , and  $\cdots \text{III}$  assemblies. The presence of this triplet–triplet absorption

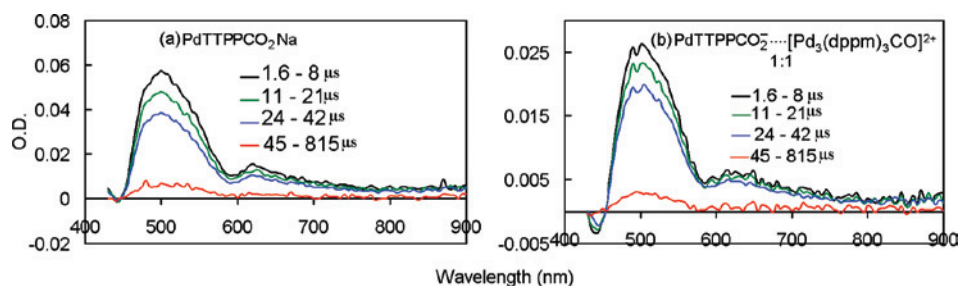
**Table 6.** Photophysical Data for the Porphyrins **I–III** and Their 1:1 Host–Guest Assemblies with  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ <sup>a</sup>

substrate in 2MeTHF at 77 K	substrate alone				1:1 $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ •••substrate				
	$\Phi^b$ (520 nm) <sup>c</sup>		$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ (ms) ( $\lambda_{\text{max}}^d$ )	$\Phi^b$ (520 nm) <sup>c</sup>		$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ (ms) ( $\lambda_{\text{max}}^d$ )	triplet $k_{\text{ET}}$ ( $\text{s}^{-1}$ )
	$\Phi_F$	$\Phi_P$			$\Phi_F$	$\Phi_P$			
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	0.039	0.013	2.73 ± 0.02 (600) <sup>d</sup>	25.95 ± 0.28 (780) <sup>d</sup>	0.037	0.011	2.69 ± 0.09 (600) <sup>d</sup>	10.40 ± 0.72 (780) <sup>d</sup>	71
ZnTTPPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	0.036	0.002	2.48 ± 0.18 (600) <sup>d</sup>	19.40 ± 0.40 (780) <sup>d</sup>	0.022	0.001	2.30 ± 0.24 (600) <sup>d</sup>	6.94 ± 0.25 (780) <sup>d</sup>	96
PdTTPPCO <sub>2</sub> <sup>−</sup> ( <b>III</b> )	>0.001	0.124	0.11 ± 0.03 (605) <sup>d</sup>	1.54 ± 0.05 (690) <sup>d</sup>	>0.001	0.103	0.15 ± 0.03 (605) <sup>d</sup>	1.40 ± 0.011 (690) <sup>d</sup>	65

substrate in 2MeTHF at 298 K	substrate alone		1:1 $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ •••substrate		
	$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ ( $\mu\text{s}$ ) ( $\lambda_{\text{max}}^d$ )	$\tau_F$ (ns) ( $\lambda_{\text{max}}^d$ )	$\tau_P$ ( $\mu\text{s}$ ) ( $\lambda_{\text{max}}^d$ )	$k_Q$ ( $\text{s}^{-1}$ )
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	0.63 ± 0.03 (605) <sup>d</sup>	<i>f</i>	0.41 ± 0.04 (605) <sup>d</sup>	<i>f</i>	8.5 × 10 <sup>8</sup> (S <sub>1</sub> )
ZnTTPPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	0.38 ± 0.04 (605) <sup>d</sup>	<i>f</i>	0.31 ± 0.04 (605) <sup>d</sup>	<i>f</i>	5.9 × 10 <sup>8</sup> (S <sub>1</sub> )
PdTTPPCO <sub>2</sub> <sup>−</sup> ( <b>III</b> )	<i>f</i>	277 ± 15 (700) <sup>d</sup>	<i>f</i>	94 ± 1 (700) <sup>d</sup>	0.70 × 10 <sup>4</sup> (T <sub>1</sub> )

<sup>a</sup> All of the emission decay traces are monoexponential. <sup>b</sup>  $\Phi_F$  and  $\Phi_P$  are reported at ±10%. <sup>c</sup> Excitation wavelength. <sup>d</sup> The values in brackets are the wavelengths where the lifetimes were measured. <sup>e</sup> There is no quenching of the fluorescence within the uncertainty. This column presents only the triplet  $k_{\text{ET}}$ . <sup>f</sup> The intensity is too weak to be measured.

**Figure 10.** Transient absorption spectra of (a) **III** and (b) 1:1 PdTTPPCO<sub>2</sub><sup>−</sup>••• $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ ,  $[\text{PdTTPPCO}_2^-] = [[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}] = 2 \times 10^{-5}$  M, in 2MeTHF at 298 K. (Spectra were measured at different delay times and  $\lambda_{\text{ex}} = 355$  nm; *x* = an artifact signal.)**Table 7.** Transient (Triplet–Triplet) Absorption Lifetimes for 1:1 Host–Guest  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ ••• $-\text{O}_2\text{CR}$  Assemblies Measured in 2MeTHF at 298 K in the Presence and Absence of O<sub>2</sub><sup>a</sup>

substrate	$\tau_{\text{T1}}$ ( $\mu\text{s}$ )					$k_Q$ ( $\text{s}^{-1}$ )
	substrate alone		1:1 $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ •••substrate			
	without O <sub>2</sub>	in the presence of O <sub>2</sub> (air)	without O <sub>2</sub>	in the presence of O <sub>2</sub> (air)		
ZnTPPCO <sub>2</sub> <sup>−</sup> ( <b>I</b> )	145	5	67	3	0.80 × 10 <sup>4</sup>	
ZnTTPPCO <sub>2</sub> <sup>−</sup> ( <b>II</b> )	137	4	55	3	1.09 × 10 <sup>4</sup>	
PdTTPPCO <sub>2</sub> ( <b>III</b> )	220	2	93	2	0.62 × 10 <sup>4</sup>	

<sup>a</sup> The uncertainties are ±5% based on multiple measurements.

band does not preclude electron transfer. This transfer can simply turn out to be slow. However, the intensity of this band as well as the ZnTPPCO<sub>2</sub>Na (**I**) system is quenched (see the SI), which makes no sense in an energy-transfer model, as suggested in Scheme 1. Because **I** and **II** are not phosphorescent at 298 K (Table 6), the triplet-state lifetimes are measured from the transient spectra (Table 7).

The  $k_Q$  values determined from the emission and transient lifetimes for the PdTTPPCO<sub>2</sub><sup>−</sup>••• $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  assembly are the same (considering the uncertainties), and the overall  $k_Q$  values for the three assemblies range from 0.6 × 10<sup>4</sup> to 1.1 × 10<sup>4</sup> s<sup>−1</sup>. Knowing that electron transfers are slow at low temperatures because of the large solvent reorganization energy and faster at warmer temperatures for the same reason, we propose that a slow photoinduced electron transfer from the metalloporphyrins to the clusters occurs. Indeed, the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster in THF is easily reduced at 0.40 V vs SCE.<sup>22</sup> On the other hand, zinc porphyrins in various solvents are oxidized with potentials of  $E^{0/1+} > +0.6$  V vs SCE.<sup>23</sup> On the basis of Figure 1, the

0–0 peak of the Q absorption band would be around 590 nm (i.e., 17 200 cm<sup>−1</sup>; ~2.1 eV). So, the driving force for photoinduced electron transfer would be at least <1.5 V vs SCE  $[\text{metalloporphyrin}]^* \rightarrow [\text{metalloporphyrin}]^+$ , which is large enough to reduce  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ . As for the reported energy transfer, the rate for electron transfer is expected to be slow because of the through-space process. Indeed, by taking the 298 K  $\tau_F$  data in Table 6, rates on the order 6 × 10<sup>8</sup>–9 × 10<sup>8</sup> s<sup>−1</sup> are calculated using eq 2, where  $k_{\text{ET}}$  is replaced by  $k_Q$ . These values lie on the slow side for electron transfers but are right in the range for supramolecular assemblies.<sup>10</sup> The question is, why do we not see any evidence for the charge-separated state in the transient absorption spectra. By examination of the reported spectra

- (22) (a) Gauthron, I.; Mugnier, Y.; Hierro, K.; Harvey, P. D. *Can. J. Chem.* **1997**, *75*, 1182–1187. (b) Brevet, D.; Lucas, D.; Catey, H.; Lemaître, F.; Mugnier, Y.; Harvey, P. D. *J. Am. Chem. Soc.* **2001**, *123*, 4340–4341. (c) Harvey, P. D.; Mugnier, Y.; Lucas, D.; Evrard, D.; Lemaître, F.; Vallat, A. *J. Cluster Sci.* **2004**, *15*, 63–90.
- (23) Kadish, K. M.; Van Caemelbecke, E. *Electrochemistry of metalloporphyrins in nonaqueous media*. In *Encyclopedia of Electrochemistry*; Bard, A. J., Stratmann, M., Eds.; Wiley: Weinheim, Germany, 2002; Chapter 9, pp 175–228.

in ref 21, again we see that the transient spectra are spread over 600–1100 nm. With the narrower triplet–triplet absorption peak, it is possible that this feature is buried under the former. No electrochemical data for the corresponding  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  are reported so far. On the basis of the lack of quenching of the reported metalloporphyrins, it is reasonably anticipated that the reduction potential may be higher than that of the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cation.

**Final Comments.** This work reports triplet energy transfers in  $[\text{M}_3(\text{dppm})_3(\text{CO})]^{2+}$ -containing assemblies held via strong electrostatic interactions, here between an unsaturated organometallic cluster cation and carboxylate-functionalized metalloporphyrins. The rate of transfer is  $10^4 \text{ s}^{-1}$  for  $[\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$ . For  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$ , no rate could be measured because of the very weak intensity of its emission. Knowing that triplet energy transfer operates according to a double electron-transfer mechanism (Dexter mechanism), then a single photoinduced electron transfer should also be possible. In this same sense, the  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  cluster exhibits two one-electron low-potential reduction processes ( $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+} + \text{e}^- \rightleftharpoons [\text{Pd}_3(\text{dppm})_3(\text{CO})]^+$  and  $[\text{Pd}_3(\text{dppm})_3(\text{CO})]^+ + \text{e}^- \rightleftharpoons [\text{Pd}_3(\text{dppm})_3(\text{CO})]^0$ ),<sup>22</sup> and the reported data in this work strongly suggested that this was indeed the case. Future work in this area is in progress.

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**Supporting Information Available:** UV–visible spectra for the electrostatic interactions of both  $\text{ZnTTPPCO}_2^-$  and  $\text{PdTTPPCO}_2^-$  with  $[\text{M}_3(\text{dppm})_3(\text{CO})]^{2+}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) and the corresponding plots used for the  $K_{11}$  calculations (Benesi-Hildebrand, Scatchard, and Scott), the emission spectra of the 1:1 assemblies of  $\text{ZnTPPCO}_2^-$  and  $\text{ZnTTPPCO}_2^-$  with  $[\text{M}_3(\text{dppm})_3(\text{CO})]^{2+}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) in 2MeTHF at 77 K as well as the emission spectra for all three 1:1 assemblies for  $\text{ZnTPPCO}_2^- \cdots$ ,  $\text{ZnTTPPCO}_2^- \cdots$ , and  $\text{PdTTPPCO}_2^- \cdots [\text{M}_3(\text{dppm})_3(\text{CO})]^{2+}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) in 2MeTHF studied at 298 K, time-resolved spectra of the 1:1  $\text{ZnTPPCO}_2^- \cdots$  and  $\text{ZnTTPPCO}_2^- \cdots [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  assemblies, triplet–triplet absorption spectra for the 1:1  $\text{ZnTPPCO}_2^- \cdots [\text{Pt}_3(\text{dppm})_3(\text{CO})]^{2+}$  and  $\cdots [\text{Pd}_3(\text{dppm})_3(\text{CO})]^{2+}$  assemblies, corrected emission spectra of  $\text{Pd}_3(\text{dppm})_3(\text{CO})^{2+}$  in 2MeTHF at 77 K in the absence and presence of acetate and benzoate, and comparison of the absorption and excitation spectra of all of the assemblies at 77 K in 2MeTHF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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